DYNAMIC OVERSTRESSES IN FIBROUS POLYMERIC MATERIALS

Robert Cook
Michael Mercer

THIS PAPER WAS PREPARED FOR SUBMITTAL TO
"MATERIALS CHEMISTRY AND PHYSICS"

November 13, 1984

CIRCULATION COPY
SUBJECT TO RECALL
IN TWO WEEKS

Lawrence Livermore National Laboratory

DISCLAIMER

Abstract

We have considered the problem of dynamic stress redistribution in fibrous materials due to the failure of a single element. Our model consists of a number of aligned adjacent chains of harmonically coupled masses. Neighboring masses on adjacent chains are also coupled by shear-carrying springs. Depending upon the scope and assignment of parameters, the model might apply to aligned polymer chains in a crystal or amorphous environment, to filaments in a fiber, or to fibrous composite materials. At time $t = 0$, an intra-chain spring is broken and the motion of the masses in the local environment is followed by molecular dynamics. The dynamic loads carried by bonds in chains neighboring the defect oscillate with decreasing amplitude, ultimately reaching asymptotic values that can also be calculated exactly by harmonic analysis. We find that the maximum of the excess load carried by a spring in a chain adjacent to a defect is about two times the asymptotic value for two-dimensional arrays of chains and somewhat larger for three-dimensional arrays. The dependence of these quantities on the magnitude of the shear-carrying spring constant is explored. These results have implications for a number of theoretical approaches to fiber and composite strength which use load-sharing models based on asymptotic values.

Introduction

The study of stress concentration around defects and its relationship to failure in materials has been an area of interest to material scientists for some time. In the area of polymeric materials a number of workers have addressed the problem from varying perspectives. One group, led by Phoenix,[1] has explored a "chain of bundles" model which focuses on the statistical nature of material failure and the consequences of various load-sharing rules. Others, such as Christensen,[2] have examined continuum models of crack growth in polymeric materials. Gotlib and co-workers[3—6] have explored a more molecular model in which they have examined stress concentration and failure in a solid polymeric material, based on the harmonic Newell-Rosenstock network model. A number of workers have also approached the problem from a kinetic point of view.[7—9] In all these studies, although they may make predictions about material lifetimes, there is an underlying assumption that between successive events the local environment completely relaxes. Specifically, stress concentrations are calculated or dealt with as static, time-independent quantities.

Studies of the actual dynamics of stress flows in polymeric materials due to the formation of a defect have been rare, though a few workers have attempted to incorporate these effects in an approximate way in studies of fibrous composite strength.[10—12]

The work most closely related to the study presented here is that of Hedgepeth[13], published as a NASA Technical Note more than twenty years ago, in which he analyzes the stress redistribution due to filament failure in a sheet of parallel filaments which carry normal loads and are embedded in a matrix which carries only shear. For this quasi-continuum model he is able to calculate the dynamic response of filaments adjacent to a newly formed defect and obtain the magnitude of the dynamic overstress, the stress in excess of that which is present when relaxation takes place.

In our work we have studied the similar discrete problem where the filaments have been replaced by chains of harmonically coupled masses and the shear acts only between mass points on neighboring chains. This discrete model is similar in some respects to that used by Gotlib and coworkers. Our motivation in studying a discrete system is to reduce the lower end of the scale of applicability of the model to the molecular level. Our molecular dynamics techniques also allow us to easily investigate the three-dimensional problem not treated by Hedgepeth. The model will be described

more fully in the next section and a comparison of our results and those of Hedgepeth will be covered in the discussion, along with other pertinent results.

Model

Our model, schematically represented in Figure 1, consists of a number of aligned adjacent chains of harmonically coupled masses. Neighboring masses on adjacent chains are also coupled by shear carrying springs. Although particle motion is purely one-dimensional along the aligned direction, we can create two-dimensional systems such as the one depicted in Figure 1 or three-dimensional arrangements of chains where each chain has six neighboring chains packed in a hexagonal array. The total energy, E_T, of the system can be expressed in terms of the spring constants A and C of the intra-chain and shear carrying springs; and the positions of the particles, $X_{j,i}$, where i indicates the position of the particle on the jth chain as

$$E_T = \frac{1}{2} \sum_{j=1}^{m} \sum_{i=1}^{n-1} A_{j,i} (X_{j,i+1} - X_{j,i} - l_0)^2$$

$$+ \frac{1}{2} \sum_{i=1}^{n} \sum_{j'=j+1}^{m} \sum_{j=1}^{m-1} C_{j',j,i} (X_{j',i} - X_{j,i})^2 \tag{1}$$

for a system with m chains of n masses each. l_0 is the unstressed bond length, set equal to unity in this work. The shear carrying spring constants $C_{j',j,i}$ are non-zero only if chains j' and j are adjacent. It should be emphasized at this point that the springs in the model need not be thought of as representing individual chemical bonds, but rather they model interactions appropriate to the scale being considered. This interpretation is particularly important for the shear-carrying springs which represent only the net resistance to relative displacement of two neighboring masses. The source of this resistance can vary from chemical cross-links to van der Waals interactions, and in the model these interactions are treated in a "mean field" manner with the magnitude governed by the value of the force constant.

The equations of motion of the mn masses are solved numerically by first calculating the forces on each particle at time t

$$F_{j,i}(t) = -\frac{\partial E_T(t)}{\partial X_{j,i}} \tag{2}$$

4

and then using the simple difference equation

$$X_{j,i}(t + \Delta t) = X_{j,i}(t) + F_{j,i}(t)\Delta t^2 + V_{j,i}(t - \frac{\Delta t}{2})\Delta t \qquad (3)$$

where

$$V_{j,i}(t - \frac{\Delta t}{2}) = \frac{X_{j,i}(t) - X_{j,i}(t - \Delta t)}{\Delta t} \qquad (4)$$

is the velocity of the particle. Particle masses have been set to unity. In the work presented here all the A-type bonds are identical, as are all the C-type bonds so the subscripts are dropped in what follows.

In order to study dynamic overstresses adjacent to a newly formed defect we initially strain the perfect system by 10% and then the $i = 1$ and n particles in each chain are held stationary. Since all bonds are harmonic with linear force laws the quantities we will examine are independent of the degree of strain. At time $t = 0$ we break(or zero) a single A bond between particles $n/2$ and $n/2 + 1$ in any chain. In setting up the array of m chains, periodic boundary conditions are used perpendicular to the aligned direction so that the initial environment of all chains is identical. The motivation and use of such boundary conditions in physical systems has been discussed by Brostow.[14] After breaking the A bond the motion of the system, and particularly the neighboring particles is followed by repeated application of Eq. (3) for sufficiently small Δt so that energy is conserved. This procedure was followed for various values of C with A set to unity to determine the dependence of the dynamics of stress redistribution on C. For the work reported here $\Delta t = 0.1$. To convert to "real" time for a system of particles of mass m connected by force constants k, one unit of time, t, would correspond to $\sqrt{m/k}$ in the time units appropriate to k. Using the appropriate constants for a polyethylene chain, one unit of time would be about 5 femtoseconds.

We also note that for large enough systems fixing the strain on the system is entirely equivalent to applying a constant stress on the end particles. This is true since the effects we are examining are local and thus do not propagate to the borders. Studies of varying sized systems has verified this fact. The specific data presented here are for two-dimensional systems which contain 40 chains of 80 particles each and three-dimensional systems with 81 chains of 50 particles each.

Results

Our primary focus is on the bonds directly adjacent to the one broken. The length of such bonds as a function of the time, t, is indicated by the solid lines in Figure 2 for $C = .50$ in two and three dimensions. The dotted lines show the "bond length" of the broken bond. Because the springs are Hookean the quantity $l(t) - l_0$ is directly proportional to the bond stress. Note the oscillatory behavior of the bond length at short time. At longer time the amplitude fades to zero as the energy is dispersed throughout the system. This asymptotic value can be calculated directly by solving the $m(n-2)$ linear equations ($i = 1, n$ particles fixed)

$$F_{j,i} = 0 \tag{5}$$

for the system with a broken bond. We quantify the overstress $\sigma_{es}(t)$ as

$$\sigma_{es}(t) = \frac{l(t) - l(0)}{l(\infty) - l(0)} \tag{6}$$

where $l(t)$ is the length of the bond at time t. Note that $l(0)$ is *not* the equilibrium value l_0 but rather the bond length immediately after imposition of the strain, but before the system has responded to the broken bond, and is thus related to the imposed load on all bonds before failure. $\sigma_{es}(t)$ thus measures the time-dependent excess load a bond near a defect carries in comparison to the load it will have when the system is completely relaxed at $t = \infty$. In Table 1 we list the values of $\sigma_{es}(t)$ at the first maximum for various values of C for the two and three dimensional systems. In the limit that C becomes very small the neighboring strand would be unaffected, however the ratio $\sigma_{es}(t)$ becomes undefined($0/0$). The decrease shown in Table 1 suggests that the value approaches unity. For very large C one would expect $\sigma_{es}(t)$ to also approach unity since adjacent masses would become locked together. We also list in Table 1 the maximum values of the dynamic response factor, η, defined by Hedgepeth as

$$\eta(t) = \frac{l(t) - l_0}{l(\infty) - l_0}. \tag{7}$$

This is simply a ratio of displacements or stresses and differs from $\sigma_{es}(t)$ by subtracting the equilibrium length, l_0, rather than the initial strained length, $l(0)$. It should be reemphasized that for a system of harmonic bonds, such as we have, the magnitude of both $\sigma_{es}(t)$ and $\eta(t)$ are independent of the initial strain. It should also be pointed out

6

that, because of the harmonic system, the values listed in Table 1 depend only on the ratio of C to A.

Discussion

Several features of the data presented in Figure 2 and Table 1 are worth noting. First, the dimensionality of the system has a significant quantitative effect on the actual motions, though qualitatively the two- and three-dimensional systems are similar. Note that in three dimensions the magnitude of the bond-length deflection is significantly reduced due to the restoring forces of the extra neighboring chains and that the first maximum occurs sooner. However the values of $\sigma_{ez}(t)$ at the first maxima are somewhat larger in three dimensions than in two dimensions due to the fact that the extra restraining forces in three dimensions are more effective at reducing $l(\infty) - l(0)$ than $l(t) - l(0)$. Note the values of both σ_{ez} and η plateau at intermediate values of C. In any physical system we would probably expect C to be some fraction of A. Thus the dynamic stress felt by a bond adjacent to a newly formed defect, opposed to one distant from it, will be roughly 1.8 times greater in two dimensions and 2.5 times greater in three dimensions. The overstress effects also extend to neighbors more distant from the defect. The ratio $\sigma_{ez}(t)$ at its maximum remains about the same, however the magnitude of the transferred stresses is much less and thus of little importance.

Our results agree qualitatively with those of Hedgepeth for his quasi-continuum two-dimensional model. He also notes oscillating behavior of the stress in neighboring filaments following the formation of a defect. Hedgepeth's calculated η for the two-dimensional system is 1.15 for unit shear constant which is to be compared with a value of 1.22 from our work. The small differences are due to the differences between a continuum and discrete model.

Some exploratory work was performed with more realistic spring potentials. Specifically, the longitudinal Hookean springs were replaced with Morse springs where the energy between adjacent masses i and $i+1$ is given by

$$E_{i,i+1}^L = D\left(\exp\left(-2\sqrt{\frac{A}{2D}}(X_{i+1} - X_i - l_0)\right) - 2\exp\left(-\sqrt{\frac{A}{2D}}(X_{i+1} - X_i - l_0)\right)\right).$$

(8)

The shear carrying springs were replaced by an inter-particle potential between adjacent masses i and j on neighboring chains as

$$E^S = -C\left(\frac{l_0}{2\pi}\right)^2 \cos\left[\frac{2\pi(X_i - X_j)}{l_0}\right] \qquad if \mid X_i - X_j \mid < \frac{X_0}{2}$$

$$E^S = 0 \qquad if \mid X_i - X_j \mid > \frac{X_0}{2}. \tag{9}$$

In both of these cases the terms have been written so that expansion to quadratic terms will give the form of Eq. (1). The parameter D, which controls the well depth, was set to .0541, which models accurately the carbon-carbon bond potential in the units at hand. Qualitatively the results are the same for this system as for the quadratic system, the quantitative agreement being better at smaller strain values as one would expect. The general pattern of an initial overstress as shown in Figure 2 remains, though the details of the relaxation are somewhat different. Since it is not possible to obtain the values of $l(\infty)$ analytically for the revised system it is difficult to get accurate values of σ_{es} and η. Qualitatively, however, the simulations show that the neighboring bond is strained more than in the harmonic case due to the softness of the Morse potential on extension. Thus, the harmonic behavior studied in this paper represents a lower bound on the magnitude of the effect.

As noted in the introduction, one area of importance of the ideas and results presented here has to do with failure theory. Use of the static stress distribution values will lead to an underestimation of the rate of failure. If the applied stress on a bond is low compared to the critical stress for failure of that bond, the effect may be of small importance since it is only a very short time effect(the order of a molecular vibration if one views the model on a molecular scale) and the probability of failure of the element is low. However, as the applied stress approaches the critical stress, the overstress will cause the local dynamic applied stress to the bond or fiber to exceed the critical value for failure, resulting in "premature" failure. Thus we conclude that it is primarily during rapid, catastrophic failure that these effects will be most important.

for some helpful comments concerning the preparation of the manuscript. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract W-7405-ENG-48.

References

1. R. E. Pitt and S. L. Phoenix, *Int. J. Fracture* 1983, 22, 243. This paper contains many references to the work of Phoenix and others on the "chain of bundles" statistical model for fiber failure.

2. R. M. Christensen, *Int. J. Fracture* 1979, 15, 3; *Int. J. Solids Structures* 1984, in press.

3. Y. Y. Gotlib and A. V. Dobrodumov, *Polymer Science USSR* 1979, 20, 962.

4. Y. Y. Gotlib, A. M. El'yashevich and Y. E. Svetlov, *Soviet Physics - Solid State* 1973, 14, 2672.

5. A. V. Dobrodumov and A. M. El'yashevich, *Soviet Physics - Solid State* 1973, 15, 1259.

6. Y. Y. Gotlib and A. V. Dobrodumov, *Polymer Science USSR* 1980, 22, 2669.

7. S. N. Zhurkov, *Vest. Akad. Nauk USSR* 1957, 11, 78; S. N. Zhurkov and S. Abasov, *Vysokomol. Soedin.* 1961, 3, 441.

8. E. Sacher, *J. Macromol. Sci.* 1978, B15, 171. This paper contains numerous useful references on the subject of kinetic models of failure.

9. R. Cook, *Polymer Comm.* 1984, 25, 246.

10. P. W. Barry, *J. Mater. Sci.* 1978, 13, 2177.

11. V. V. Moskvitin and V. V. Moskvitin, *Mech. Solids* 1983, 18, 114.

12. P. W. Manders and T. Chou, *J. Compos. Mater.* 1983, 17, 26.

13. J. M. Hedgepeth, *NASA Technical Note* 1961, TN-D-882.

14. W. Brostow, *Science of Materials*, Wiley, New York, 1979. See section 11.3.

Table 1. The values of the dynamic overstresses, σ_{es}, and dynamic response factors, η, are given at their maxima for the two-dimensional($2D$) and three-dimensional($3D$) systems as a function of the shear-carrying force constant, C.

C	σ_{es}^{2D}	σ_{es}^{3D}	η^{2D}	η^{3D}
0.10	1.61	1.78	1.15	1.07
0.20	1.70	2.17	1.17	1.10
0.30	1.58	2.37	1.14	1.11
0.40	1.68	2.47	1.16	1.11
0.50	1.78	2.52	1.18	1.11
0.60	1.86	2.54	1.19	1.11
0.70	1.91	2.55	1.20	1.10
0.80	1.95	2.54	1.21	1.10
0.90	1.99	2.52	1.21	1.10
1.00	2.01	2.50	1.22	1.09
1.20	2.04	2.46	1.22	1.08
1.40	2.05	2.41	1.22	1.08
1.60	2.05	2.37	1.21	1.07
1.80	2.05	2.31	1.21	1.07
2.00	2.04	2.27	1.20	1.06
3.00	1.96	2.05	1.17	1.04
5.00	1.78	1.76	1.12	1.03
10.00	1.56	1.63	1.07	1.02

Figure 1. The model under study. Motion of the masses is restricted to the horizontal direction. The masses in adjacent horizontal chains are linked by shear-carrying springs.

Figure 2. Bond lengths of the broken bond(dotted) and adjacent bond(solid) are given as a function of time for two dimensional (2-D) and three dimensional (3-D) systems for $C = .5$. The bond is broken at $t = 0$ and the initial strain is 10%.
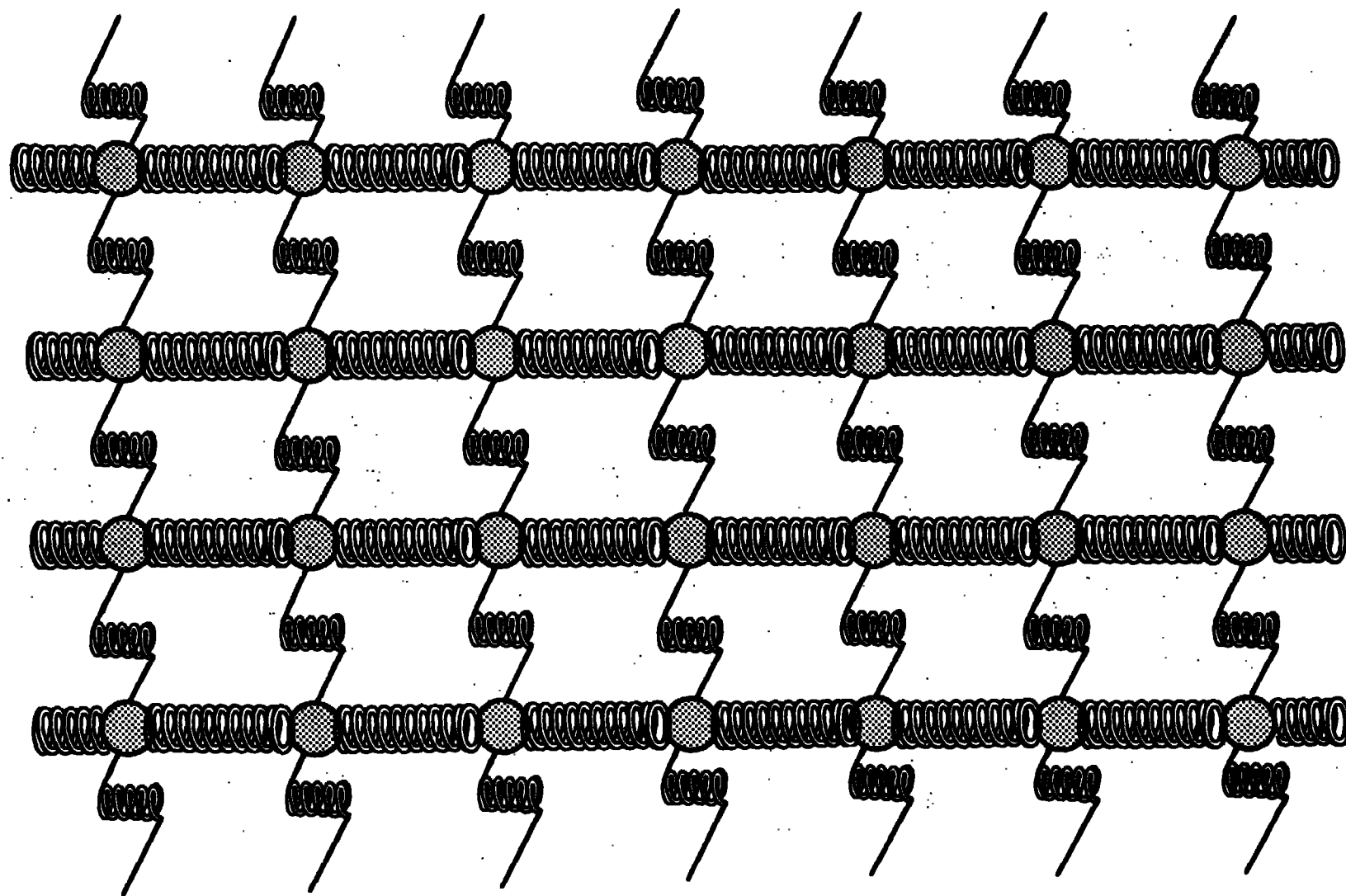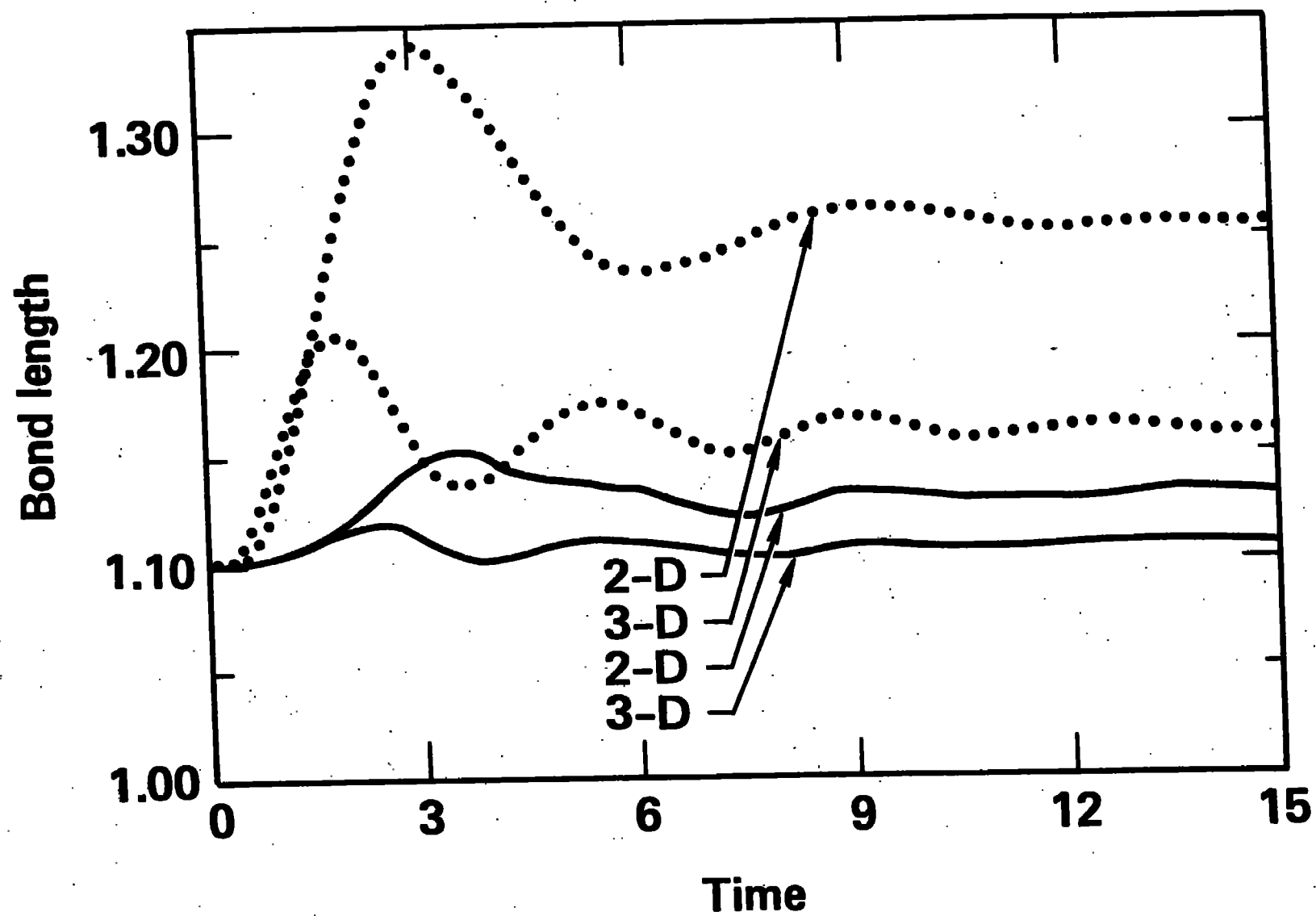
FIGURE 1

FIGURE 2